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VIBRATIONAL SPECTRA, APPROXIMATE POTENTIAL CONSTANTS AND CALCULATED THERMODYNAMIC PROPERTIES OF BENZOPHENONE

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ABSTRACT. Benzophenone has been subjected to normal coordinate treatment assuming the phenyl groups to be point masses. The Wilson *F-G* matrix method has been employed to obtain the secular equation in order to calculate the fundamental frequencies. In calculating the thermodynamic properties, contributions from the ring frequencies are also included.

INTRODUCTION

The infrared spectrum of benzophenone is not found in literature in all its aspects, although several workers mention the carbonyl frequency. However, the Raman spectrum of benzophenone has been recorded among others by Kohlrausch and Pongratz (1934), Lestrade (1952) and Puranik (1953). No attempt appears to have been made to subject the molecule to normal coordinate treatment.

EXPERIMENTAL

The infrared spectrum was recorded with a Perkin-Elmer Infrared Spectrophotometer Model 21 with NaCl optics. The spectrum was recorded in nujol mull and in solutions of CCl_4. The spectrum in solutions of CCl_4 was more extensive but it did not exhibit any shift in the frequencies recorded in the mull.

The Raman spectrum of molten benzophenone was recorded by using a Hilger Raman Source Unit and Fuess Glass Spectrograph having a dispersion of 19 Å/mm in λ4358 region. In order to get the spectrum of molten benzophenone, the melt is poured in the Raman tube in the Unit and the flow of the cooling water circulation is slowed down and regulated so as to keep the temperature of the cell slightly above 49°C which is the melting point of benzophenone. In this way the substance can be retained in molten state for a considerable time.

Benzophenone of Merck make was recrystallised by dissolving it in anhydrous absolute ethyl alcohol.

RESULTS

The Raman spectrum of benzophenone melt and its infrared spectrum in solutions in CCl_4 are given in Table 1. The Raman spectrum of the substance as

recorded by Lestrade is given for comparison. The present results, however, agree more closely with those reported by Kohlrausch and Pongratz. The assignments proposed are also indicated in Table I.

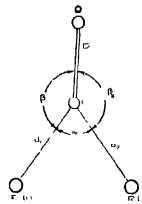
TABLE I

Raman and infrared frequencies in cm^{-1}

Raman		Infrared	Assignments
Authors	Lestrade	Authors	
148 (2)	--	—	
221 (2)	223 (5)	--	
277 (2)	--	--	R-C-R deformation.
—	387 (1)	—	
406 (2)	410 (1)	—	C (e_{2u}) ring
567 (2)	559 (1)	—	C-C=O deformation.
--	579 (2)	—	
616 (3)	612 (5)	—	C (e_{2g}) ring.
—	—	699 (s)	C-H out-of-plane bending.
721 (2)	—	717 (m)	
764 (2)	--	—	
810 (1)	—	—	
845 (2)	—	845 (w)	
—	—	917 (s)	C-H out-of-plane bending.
—	943 (1)	939 (m)	
—	--	971 (w)	1674−699=975.
1003 (5)	996 (10)	—	C-C (a_{2g}) ring.
1027 (3)	1023 (3)	1028 (m)	
			C-H in-plane bending.
		1136 (m)	
1151 (4b)	1155 (5)	1148 (m)	C-R symmetric stretch.
		1176 (w)	559+612=1171,
		1220 (w)	
		1249 (w)	845+406=1251.
1281 (1)	1282 (3)	1274 (vs)	C-R antisymmetric stretch.
--		1307 (s)	
1322 (1)		1316 (s)	1600−277=1328.
—		1389 (w)	1603−221=1382.
1448 (0)	1451 (1)	1449 (s)	1600−148=1452.
—	—	1475 (sh)	
1492 (0)	1491 (1)	1493 (m)	721+764=1485.
	1542 (1)		
	1578 (1)	1581 (m)	ring.
1600 (7)	1600 (10)	1603 (s)	C=C stretch.
1658 (5)	1661 (5)	1674 (vs)	C=O stretch.
—	—	1689 (w)	2×845=1690.
3052 (2b)	—	3053 (w)	C-H stretch.

NORMAL COORDINATE TREATMENT

If the phenyl groups in benzophenone are assumed to be point masses the molecule can be treated as a four body problem having the symmetry of the point group C_{2v} with a distribution $(3A_1, 2B_1, B_2)$. All the normal vibrations are both Raman and infrared active. The Normal coordinate treatment has been carried out by the authors according to the Wilson F-G matrix method. The following symbols are used for the equilibrium values of bond distances and interbond angles which are shown in the Fig. 1.



R = C_6H_5

Fig. 1

In accordance with the above notation an example of the possible types of the potential constants arising out of different interactions are :

f_d = C-R stretching constant.

f_α = ∠RCR bending constant.

$f_{\alpha D}$ = ∠RCR and C = O angle bond interaction constant.

$f'_{d\beta}$ = C-R and ∠OCR bond-angle interaction constant, the prime indicating that the bond and the angle do not have a common bond.

The most general quadratic expression for the potential energy has the coefficients given in Table II.

TABLE II

	ΔD	Δd_1	Δd_2	$\Delta\alpha$	$\Delta\beta_1$	$\Delta\beta_2$
ΔD	f_D	f_{Dd}	f_{Dd}	$f_{D\alpha}$	$f_{D\beta}$	$f_{D\beta}$
Δd_1		f_d	f_{dd}	$f_{d\alpha}$	$f'_{d\beta}$	$f_{d\beta}$
Δd_2			f_d	$f_{d\alpha}$	$f_{d\beta}$	$f'_{d\beta}$
$\Delta\alpha$				f_α	$f_{\alpha\beta}$	$f_{\alpha\beta}$
$\Delta\beta_1$					f_β	$f_{\beta\beta}$
$\Delta\beta_2$						f_β

The symmetry coordinates for the

Type A_1

$$R_1 = \Delta D.$$
$$R_2 = 1/\sqrt{2}(\Delta d_1 + \Delta d_2).$$
$$R_3 = 1/\sqrt{6}(2\Delta\alpha - \Delta\beta_1 - \Delta\beta_2).$$

Type B_1

$$R_4 = 1/\sqrt{2}(\Delta d_1 - \Delta d_2).$$
$$R_5 = 1/\sqrt{2}(\Delta\beta_1 - \Delta\beta_2)$$

The symmetry coordinates are normalised and orthogonal. From the potential energy matrix and the matrix formed from the coefficients contained in the symmetry coordinates the F matrix elements are formed. The F matrices are as follows. For type A_1

$$\begin{pmatrix} F_{11} & F_{12} & F_{13} \\ & F_{22} & F_{23} \\ & & F_{33} \end{pmatrix} = \begin{pmatrix} f_D & \sqrt{2}f_{Dd} & \sqrt{(2/3)}(f_{D\alpha} - f_{D\beta}) \\ & f_d + f_{dd} & 1\sqrt{3}(2f_{d\alpha} - f_{d\beta} - f'_{d\beta}) \\ & & 1/3d^2(2f_\alpha + f_\beta + f_{\beta\beta} - 4f_{\beta\alpha} \end{pmatrix}$$

For type B_1

$$\begin{pmatrix} F_{44} & F_{45} \\ & F_{55} \end{pmatrix} = \begin{pmatrix} f_d & f_{dd} & f_{d\beta} - f'_{d\beta} \\ & & f_\beta - f_{\beta\beta} \end{pmatrix}$$

The structural parameters of benzophenone were not available to the authors, either from X-ray or electron diffraction data. However, the values of bond distances given by Karl Hauptman *et al.* (1957) for *p-p* dimethoxy benzophenone and the value of inter bond angles given by Glasston (1935) are found suitable for the molecule under investigation in calculating the G matrix elements. These values are :

C—R = 1.46 Å, C — O — 1.3 Å, $\angle$RCR = 131° and $\angle$O = C—R = 114°30′. The elements of G matrices were evaluated with the help of Decius (1948) Tables. The actual values of the elements of G matrices for classes A_1 and B_1 are given below. The out of plane vibrations falling under the class B_2 have not been discussed in this paper.

$$\begin{pmatrix} G_{11} & G_{12} & G_{13} \\ & G_{22} & G_{23} \\ & & G_{33} \end{pmatrix} = \begin{pmatrix} 8{\cdot}7820\times10^{22} & -2{\cdot}9418\times10^{22} & 7{\cdot}6582\times10^{30} \\ & 2{\cdot}5067\times10^{22} & -4{\cdot}4914\times10^{30} \\ & & 1.2791\times10^{39} \end{pmatrix}$$

$$\begin{pmatrix} G_{44} & G_{45} \\ & G_{55} \end{pmatrix} = \begin{pmatrix} 9{\cdot}0887\times10^{22} & -9{\cdot}5886\times10^{30} \\ & 1{\cdot}5856\times10^{39} \end{pmatrix}$$

The potential constants for the molecules having similar structures as benzophenone were transferred to this molecule. Probably in view of the fact that the phenyl groups are assumed to be point masses the bond-angle and the angle-angle interaction terms were very critical. After a few modifications the observed frequencies were reproduced by calculations, the difference in their values being well within one per cent. The potential constants* thus finally arrived at are $f_D = 13.0$, $f_d = 7.25$, $f_\alpha = 1.5$, $f_\beta = 1.73$, $f_{dd} = 2.75$, $f_{d\alpha} = -1.5$, $f_{d\beta} = 1.17$, $f'_{d\beta} = 0.626$, $f_{D\alpha} = 1.2$, $f_{D\beta} = -2.0$, $f_{\alpha\beta} = -0.4$ and $f_{\beta\beta} = -0.33$.

The observed and the calculated values of the frequencies of the normal vibrations considering the phenyl group to be a point mass are given in Table III.

TABLE III

Type	observed		Calculated
	Raman	Infrared	
	1658	1674	1664
A_1	1151	1148	1150
	277	—	273
B_1	1281	1274	1278
	567	—	561

THERMODYNAMIC PROPERTIES

The heat content, free energy, entropy and heat capacity at constant pressure for benzophenone with rigid rotator and harmonic oscillator approximation have been calculated. The contributions from the normal vibrations discussed in this paper and the contributions from the rmg frequencies are included in calculating the thermodynamic properties, for the ideal gaseous state at one atmospheric pressure for twelve temperatures in 100-1000°K range. Since no data were available for the vibrational frequencies in the gaseous state of the molecule, the observed values as recorded by the authors are used. The thermodynamic properties are given in Table IV.

*Bond constants and bond-bond interaction constants are given in md/A, bond-angle interaction terms in md/rad, angle constants and angle-angle interaction constants are given in mdA/rad².

TABLE IV

Heat content, free energy, entropy and heat capacity for benzophenone

T°K	$(H_0 - E^\circ_0)/T$	$-(F - E^\circ_0)/T$	S°	C_p°
100	9 01	50.78	59 79	11.30
200	11.76	57 82	69 58	18 07
273	14 12	61.81	75 95	23.57
303	15 33	63 35	78 68	26 65
400	19 11	67 73	87 51	33 51
500	22 90	71 75	95 98	40.30
600	26 62	75 39	104 01	46 87
700	29 51	80.23	111.24	50 43
800	32 33	84 89	118 23	53.83
900	35 12	89 44	125 09	57 12
1000	37 86	93.85	131 71	62 33

N. B The moments of inertia of the molecule in a.w.u.A^2 are $I_x = 54.945$, $I_y = 272.194$ and $I_z = 327.130$. The temperatures are given in K and the other quantities are in cal. deg^{-1} $mole^{-1}$.

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